Optical properties of potassium erbium double tungstate $KEr(WO_4)_2$

T.Zayarnyuk[1*], M.T.Borowiec[1*], V.Dyakonov[1,2], H.Szymczak[1], E.Zubov[1,2], A.Pavlyuk[3], M.Barański[1]

[1]Institute of Physics, Polish Academy of Sciences, al.Lotników 32/46, 02-668 Warsaw, Poland
[2]A.A.Galkin Donetsk Physico-Technical Institute, 340114 Donetsk, Ukraine
[3]Institute of Inorganic Chemistry, 630095 Novosibirsk, Russia

ABSTRACT

Results of spectroscopic investigations of crystalline potassium-erbium double tungstate $KEr(WO_4)_2$ are reported. The single crystals of $KEr(WO_4)_2$ were grown by Top Seeded Solution Growth (TSSG) technique. They belong to the chain-layered group of materials crystallizing in monoclinic syngony (space group C^6_{2h}-C2/c). The investigations were carried out in the broad spectral and temperature range (temperature range from 1.1K up to room temperature and the spectral range from 6000 cm^{-1} to 25000 cm^{-1}). It was found that the potassium erbium double tungstate belong to the class of the diaxial crystals and it is a pleochroic. The main optical absorption spectra are determined.

Keywords: rare-earth double tungstate; pleochroism, optical absorption spectra, biaxial crystals, index of refraction

1. INTRODUCTION

Investigations of physical properties of the rare earth-alkali metal double tungstates are of interest both from scientific and practical point of view. Their studies are strongly stimulated first of all by possible applications of these compounds as active materials in solid state lasers[1]. Another very important possible application of rare earth double tungstates is using them as cooling agents in an adiabatic demagnetization method for obtaining very low temperatures[2]. From scientific point of view main considered problems are possible phase transitions as well structural as magnetic ones and the interaction between rare earth ions responsible for phase transitions. Dysprosium alkali metal double tungstates are currently a topic of intensive study[3]. These compounds are interesting by virtue of structural phase transitions that take place in them in the presence of complex magnetic ordering at subkelvins region[4]. The studies of the structural phase transition caused by the cooperative Jahn-Teller effect (CJTE) are of the significant interest. They are directed to establish the mechanism responsible for phase states and symmetry in real crystals. The detailed study of the structural phase transitions of the CJTE type shows that these occur in compounds composed of ions having two closely spaced energetic levels as a ground state.

In this paper we present optical properties of $KEr(WO_4)_2$. The spectra of erbium ions (Er^{3+}) in crystals give information on the optical and other physical properties. The potassium-erbium double tungstate crystalises in α-$KY(WO_4)_2$ structure in monoclinic space group C^6_{2h}-C2/c [5] with cell parameters a=8.03 Å, b=10.29 Å, c=7.51 Å, β=94° [5]. The structure is characteristic for several others rare earth double tungstates and belongs to the chain-layered systems. The erbium ion is surrounded by eight oxygen ions and it is placed on C_2 point symmetry site. Because of low symmetry of the $KEr(WO_4)_2$ single crystals many physical properties are highly anisotropic. For C^6_{2h} symmetry double refraction and plechroism are expected.

2. EXPERIMENTAL TECHNIQUES

The double tungstates of the general formula $MRe(WO_4)_2$, where M is an alkaline ion, Re - rare-earth ion, undergo irreversible structural phase transitions at temperatures slightly below their melting points. This phenomenon does not allow obtaining low temperature phases of these compounds by means of the Czochralski technique despite their congruent melting. To lower the temperature of crystallisation below the temperature of the phase transition High Temperature Solution Growth (HTSG) technique is used. In case of $KEr(WO_4)_2$ single crystal growth $K_2W_2O_7$ was used as a solvent due

*MTB - e-mail: borow@ifpan.edu.pl; mkpbor@it.com.pl
TZ - e-mail: zayar@ifpan.edu.pl

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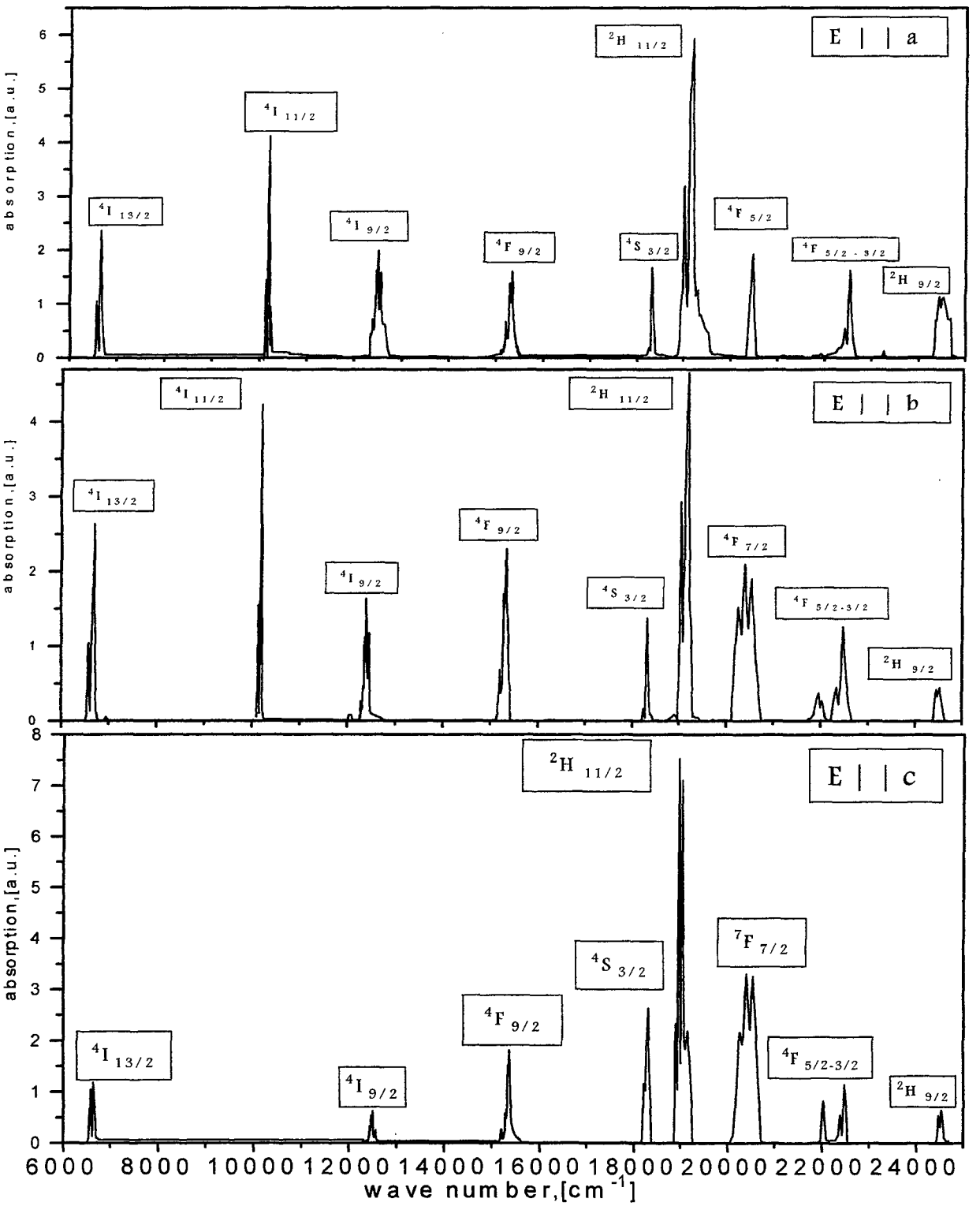

Fig1. The main optical absorption spectra of $KEr(WO_4)_2$ are connected with $4f^{11}$electron configuration of Er^{3+} ions. Ground state multiplet for Er^{3+} ions is $^4I_{5/2}$. The next multiplets are $^4I_{3/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{5/2}$,. $^4F_{3/2}$, $^2F_{5/2}$, $^2H_{9/2}$. Figure presents optical transitons to all above excited multiplets at temperature 1.1 K.

to its low viscosity and good solubility of double tungstates. The single crystals were grown by the TSSG technique on oriented $KEr(WO_4)_2$ seeds, which were obtained by means of spontaneous crystallisation from solutions of $KEr(WO_4)_2$ in $K_2W_2O_7$. For optical investigations the single crystals of $KEr(WO_4)_2$ were cut and polished to form of plates with different orientation of flat surface. The orientation of plates was established by the X-ray diffraction method.

Optical spectra were determined in two different cryogenic systems working globally in temperature range between 1.1 K and 500 K from which the range between 1.1 K to 300 K was used. First cryogenic system based on the Oxford Instrument Cryostat CF1104 working from 3.5 K to 500 K with programmable controller ITC4 necessary to set the temperature sweep and hold parameters. The second one was composed mainly from the cryostat of own production, reducing temperature down to 1.1 K.

The optical signal was measured by phase-sensitive method using the Princeton Applied Research (PAR) Lock-In Amplifier - model 5209. Two monochromator systems were used. One working mainly in VIS spectral region based on Carl Zeiss Jena double grating monochromator Model GDM 1000. Second one working also in NIR spectral region up to 6 μm was made from Carl Zeiss Jena monochromator Model SPM2 with changeable different dispersion elements (set of prisms and gratings). To detection of light three different detectors were used - for VIS region two different photomultipliers with the S20 spectra response photocathode and with the GaAs-photocathode and for NIR region the PbS detector. In summary the optical spectra were measured in broad spectral range from 6000 cm^{-1} to 25000 cm^{-1}. The full experimental systems were controlled by the computer DTC-8 with suitable hardware and software.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Because of low symmetry (C^6_{2h}-C2/c) of the $KEr(WO_4)_2$ single crystal also its optical properties are highly anisotropic. In particular, the potassium erbium double tungstate belongs to the optical class of biaxial crystals. Using optical methods, the orientations of optical axes (main axes of indicatrix) at 300 K have been found. The optical (**a**, **b**, and **c**) and the crystallographic (**x**, **y** and **z**) axes are different with one exception of the optical axis **b** which is identical with the crystallographic axis **y**. The angles between the optical axes **a** and **c** and the crystallographic axes **x** and **z** were determined experimentally (the angle between the optical axis **a** and the crystallographic axis **x** is equal 17°). Using microscopy method the main refractive indexes have been measured at 300 K. The experimentally obtained values are following: n_a= 2.881±0.084, n_b= 1.205±0.011, n_c= 4.438±0.040.

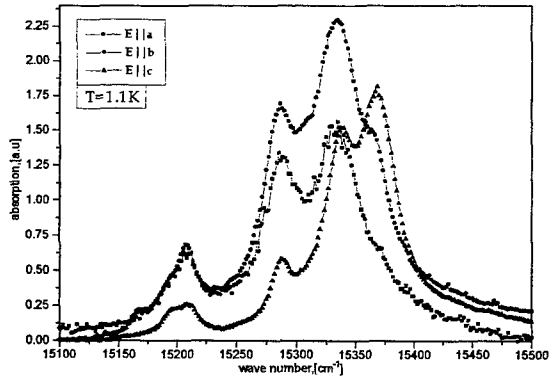

Fig. 2. The main optical absorption spectra of $KEr(WO_4)_2$ at temperature 1.1 K in the region 15100 cm^{-1}-15500 cm^{-1}.

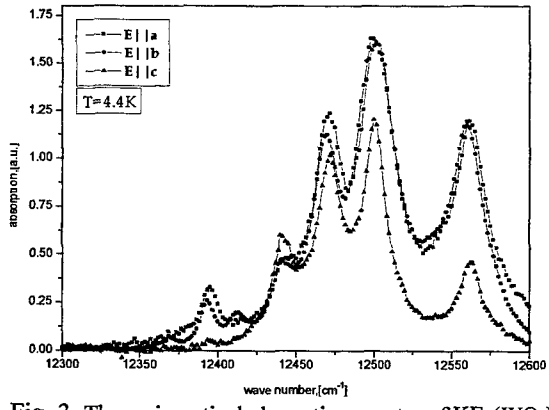

Fig. 3. The main optical absorption spectra of $KEr(WO_4)_2$ at temperature 4.4 K in the region 12300 cm^{-1}-12600 cm^{-1}.

The investigations of absorption spectrum of $KEr(WO_4)_2$ single crystals were performed in a wide spectral range (6000 cm^{-1} - 25000 cm^{-1}) at temperature from 1.1 K up to 300 K. The trichroism of $KEr(WO_4)_2$ was found experimentally, that means the optical absorption is characterized by three different, independent spectra attributed to three optical axes (so called main optical spectra). Fig. 1 presents three main optical spectra at temperature 1.1 K for electrical vector of linearly polarized light parallel to **a**,**b**,**c** optical axes, respectively. The presented spectra are composed of several groups of narrow lines in the same spectral regions (and in the same order) similarly to the spectrum of free Er^{3+} ion [6]. The

differences in intensities and number of lines between individual main spectra in particular spectral regions should be underlined. It is a simple manifestation of pleochroic (trichroic) properties of the erbium-potassium double tungstate.

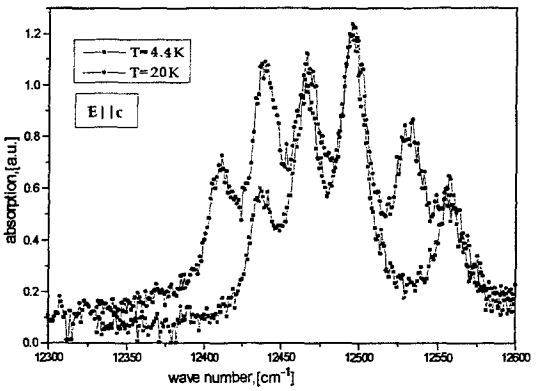

Fig. 4. The main optical absorption spectra of $KEr(WO_4)_2$ at temperature 4.4 K and 20 K in the region 12300 cm^{-1} - 12600 cm^{-1}.

Figs. 2 and 3 present main optical absorption spectra in details for two arbitrary selected spectral regions: from 15100 cm^{-1} to 15500 cm^{-1} and from 12300 cm^{-1} to 12600 cm^{-1}. In the Fig. 2 it is clearly seen that observed three main spectra are different.

With temperature increase the optical spectra become more complicated. There are observed thermal satellites on low energy side - for example in the Fig. 3 in the region of about 12440 cm^{-1}. Fig. 4 presents the comparison of the optical spectra with strongly resolved thermal satellites at higher temperatures (the spectra at 4.4 K and 20 K). The presence of the observed thermal satellites up to 300 K allows to divide all satellites into three groups with different energy distances to high-energy lines. The lowest experimentally found distance between thermal satellites and high-energy lines is equal to about 27 cm^{-1}.

The above presented main optical absorption spectra of $KEr(WO_4)_2$ are connected with $4f^{11}$ electron configuration of Er^{3+} ions. Ground state multiplet for Er^{3+} ions is $^4I_{15/2}$. The next multiplets for free Er^{3+} ions are $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{5/2}$,. $^4F_{3/2}$, $^2F_{5/2}$, $^2H_{9/2}$. From the Fig. 1 it was found that they are observed the optical transitons to all above excited multiplets. In low symmetry crystal field the ground multiplet $^4I_{15/2}$ is split in 8 Kramers doublets. The above described thermal dependences of spectra allow to estimate the energy distance between two lowest Kramers doublet to be about 27 cm^{-1}.

4. CONCLUSIONS

The double tungstate $KEr(WO_4)_2$ has unusual optical properties and it is both biaxial (double refraction) and trichroic (pleochroism). The observed spectra are connected with f^{11} configuration of Er^{3+} ions. The ground term for Er^{3+} ion is $^4I_{15/2}$. In low symmetry crystal field this term is split into 8 Kramers doublets. The observed temperature dependences of optical absorption spectra are explained in terms of the transitions from first, second and third excited states.

ACKNOWLEDGMENTS

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